Novel high-K inverse silver oxide phases of SiO$_2$, GeO$_2$, SnO$_2$, and their alloys

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Abstract

The recently reported inverse silver oxide phase of SiO$_2$ possesses a high dielectric constant as well as lattice constant compatibility to Si. We explore the closely related oxides, GeO$_2$, SnO$_2$ with the same inverse silver oxide structure using ab initio density functional theory within the local density approximation (LDA). According to the phonon dispersion curves, both these structures are computed to be unstable. On the other hand, their alloys Si$_{0.5}$Ge$_{0.5}$O$_2$, Si$_{0.5}$Sn$_{0.5}$O$_2$, and Ge$_{0.5}$Sn$_{0.5}$O$_2$ are stable with higher dielectric constants than that of SiO$_2$ in the same phase. Their first-principles elastic constants, electronic band structures and phonon dispersion curves have been obtained with high precision.

Keywords: Ab initio electronical and structural calculation; Inverse Ag$_2$O (silver oxide) phase; High dielectric constant materials; Elastic properties

1. Introduction

The search for high-dielectric constant (high-K) oxides is proceeding in several fronts, such as the consideration of transition-metal oxides like TiO$_2$, ZrO$_2$, and HfO$_2$. In the case of crystalline oxides, there is the additional possibility to search for advantageous polymorphs of the well-known oxides. Very recently, Ouyang and Ching [1] have reported a high-density cubic polymorph of SiO$_2$ in the inverse Ag$_2$O structure, named by them the “i-phase”, possessing both high-K and lattice constant compatibility to Si(1 0 0) surfaces. For gate oxide applications, crystallization of high-K materials is in general undesirable since a poly-crystalline oxide will cause higher leakage currents and introduce new diffusion paths for dopants due to its grain boundaries [2]. On the other hand, a crystalline oxide grown epitaxially on Si can also be favorable as it will possibly result in a high interface quality. Particularly interesting would be a crystalline SiO$_2$ phase with a good lattice match to Si and a higher dielectric constant than that of amorphous SiO$_2$.

In this computational study, we continue this search for the crystalline high-K oxides with the i-phases of GeO$_2$ and SnO$_2$ as well as their ternary alloys including SiO$_2$. We employ the well-established ab initio framework based on the density functional theory within local density approximation (LDA) using pseudopotentials and a plane wave basis [3]. The mechanical stability of each material is checked using their computed elastic constants as well as with the phonon dispersion curves.
2. Computational details

The simple cubic $X_{0.5}Y_{0.5}O_2$ polymorph in the inverse $Ag_2O$ structure is shown in Fig. 1. The space group for the compounds, SiO$_2$, GeO$_2$ and SnO$_2$ is $Pn\bar{3}m$ and for their alloys $X_{0.5}Y_{0.5}O_2$ it becomes $P43m$. The structural and electronic properties of the i-phase structures under consideration have been calculated within the density functional theory [3], using the plane wave basis pseudopotential method as implemented in the ABINIT code [4]. The results are obtained under the LDA where for the exchange-correlation interactions we use the Perdew–Zunger [6] (which in turn reproduces the quantum Monte Carlo electron gas data of Ceperley and Alder [7]). We tested the results under two different norm-conserving Troullier and Martins [8] type pseudopotentials, which were generated by A. Khein and D.C. Allan (KA) and Fritz Haber Institute (FHI). In the course of computations, the plane wave energy cutoff and $k$-point sampling were chosen to assure a 0.001 eV energy convergence for all i-phase crystals. Phonon dispersions and phonon density of states (DOS) were computed by the PHON program [9] using a $2\times2\times2$ supercell of 48 atoms to construct the dynamical matrix. The required forces were extracted from ABINIT.

3. First-principles results

The lattice constants and other structural informations of all i-phase crystals are listed in Table 1.

![Fig. 1. Ball and stick model of $X_{0.5}Y_{0.5}O_2$.](image)

The lattice constant of the Si(001) surface is about 3.83 Å, therefore according to LDA results Si$_{0.5}$Ge$_{0.5}$O$_2$ is particularly favorable as it can be epitaxially grown on Si(100) without any strain. Using XO$_2$ and X$_{0.5}$Y$_{0.5}$O$_2$ for the generic notation of these i-phase crystals, we note that the O–X–O and O–Y–O bond angles are 109.47° and the X–O–X and X–O–Y bond angles are 180°. The elastic constants and dielectric permittivity tensor of each i-phase crystal are tabulated in Tables 2 and 3, respectively. The band structures for the compounds and ternary alloy crystals as obtained with KA pseudopotentials are displayed along the high-symmetry lines in Figs. 2 and 3 and the corresponding total DOS are shown in Figs. 4 and 5.

For all of the i-phase crystals under consideration the conduction band minima occur at the $\Gamma$ point, whereas the valence band maxima are located at $R$ point making them indirect band gap materials.
However, the direct band gap values are only marginally above the indirect band gap values. A renown artifact of LDA for semiconductors and insulators is the underestimation of the true band gap values [3]. In this work we do not attempt any correction procedure to adjust the LDA band gap values. After these general comments, now we report the results of each lattice individually.

The simple cubic SiO$_2$ polymorph with the inverse Ag$_2$O structure (i-SiO$_2$) containing two molecules within the primitive cell has been very recently proposed by Ouyang and Ching [1]. The wide band gap, unusually high dielectric constant as in stishovite SiO$_2$ and the lattice constant compatibility to Si make this phase very attractive for electronic applications. We computed the electronic and structural properties of i-SiO$_2$ by using 65 Ha plane wave energy cutoff and 10 $\times$ 10 $\times$ 10 $k$-point sampling. The computed band structure and the total DOS of the i-SiO$_2$ shown in Fig. 2(a) and 4(a) are in good agreement with Ouyang and Ching [1]. Elastic constants and dielectric constants of the crystal are listed in Tables 2 and 3, respectively.
Motivated by the appealing features of i-SiO2, we consider the electronic and structural properties of i-GeO2, i-SnO2 and their ternary alloys: Ge0.5Si0.5O2, Ge0.5Sn0.5O2 and Sn0.5Si0.5O2. The plane wave energy cutoff and $k$-point sampling were chosen to get 0.001 eV energy convergence.

The band structure and the DOS of i-phase crystals GeO2 and SnO2 can be seen in Figs. 2 and 4, respectively. An important concern is whether these cubic phases of SiO2, GeO2 and SnO2 are stable or not. The requirement of mechanical stability in a cubic crystal leads to the following restrictions on the elastic constants:

$$C_{11} \geq C_{12}, \quad C_{11} \leq 0, \quad C_{44} \leq 0, \quad \text{and} \quad C_{11} + 2C_{12} > 0.$$ 

The elastic constants in Table 2 satisfy these stability conditions.

Furthermore, we compute the phonon dispersion curves of these structures. It can be inferred from Fig. 6 that i-SiO2 is at least locally stable whereas i-GeO2 and i-SnO2 contain negative phonon branches which signal an instability of these phases.

The band structures and the DOS of i-phase Ge0.5Si0.5O2, Ge0.5Sn0.5O2 and Sn0.5Si0.5O2 are shown in Figs. 3 and 5, respectively. The ternary alloy elastic constants listed in Table 2 also satisfy the mechanical stability conditions.

The computed phonon dispersion curves of these structures are locally stable as can be observed in Fig. 7.

### 4. Conclusions

Crystalline oxides can be considered as Si CMOS gate oxides if they can be lattice matched to Si, so that a high quality interface is obtained. In this respect, the i-phases of SiO2, Si0.5Ge0.5O2, Si0.5Sn0.5O2 are particularly promising with their high dielectric constants besides their lattice match to Si, especially in the case of Si0.5Ge0.5O2.

Furthermore, first-principles elastic constants, electronic band structures and phonon dispersion curves of these i-phase oxides have been obtained with high accuracy in this work. Given the phonon dispersion curves, GeO2 and SnO2 are predicted to
be unstable, while their alloys turn out to be stable within LDA; this needs to be tested with other approaches such as the generalized gradient approximation [3]. Finally, we note that we do not consider the thermodynamic stability of these i-phase oxides. Also, we should mention that for technological applications the epitaxial growth conditions become more critical as opposed to bulk system stability. A promising direction for further theoretical studies can be the finite temperature investigation of these i-phase isovalent structures on Si(100) surfaces using large number of monolayers.

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References